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Dielectric Parameters of Polystyrene / Fullerene Composite Films

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The paper describes the frequency dependences of the electrophysical parameters (capacitance, dielectric constant, dielectric loss tangent, and resistivity) of polystyrene films filled with small additions of fullerenes (up to 1 wt % of C_{60}). The composite materials obtained were concluded to be nonpolar. The dielectric constant as a function of the film composition passes through a minimum at 0.035 wt % of C_{60}. The polymer maintains good insulating properties when filled with fullerenes.

Keywords: Polystyrene, Fullerenes, Dielectric permittivity, Dielectric loss, Conductivity.

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1. INTRODUCTION

The development of polymeric nanocomposites with controllable structure and properties is one of priority lines of the modern chemistry and materials science. Harsh conditions of polymer operation in power engineering and in chemical, petroleum, and pulp-and-paper industries impose stringent requirements upon the properties of the polymers such as hardness, strength, and electrophysical parameters. Doping of polymers with fullerenes improves the physicochemical and operation characteristics of the materials.

One of the first polymers modified with fullerenes was polystyrene (PS). Its macromolecules are capable to bind C_{60}. Because of the absence of polar groups, the electrical conductivity of polystyrene is extremely low (no more than 10^{-14} $Ohm^{-1}\cdot m^{-1}$) [1], which makes extensive use of it, e.g., in production of capacitors, of casings for household devices, and of insulation for current leads.

It should be noted that doping with fullerenes inhibits thermal degradation of the polymer and imparts to it antimicrobial properties. In particular, zones of inactivation of *St. Aureus* and *E. Coli* bacteria around samples of polystyrene films modified with C_{60} were revealed (Fig. 1) [2]. Therefore, fullerene-containing composite materials show much promise in production of medical devices and of items for household and sanitation purposes.

However, doping of polystyrene with fullerenes can deteriorate its dielectric characteristics. In particular, Adamopoulos et al. [3] studied the electrical properties of thin polystyrene films doped with 23-60 wt % of C_{60}. They found that an increase in the fullerene concentration leads to a monotonic increase in the high-frequency dielectric constant of the material from 2.4 to 2.8 and to a considerable increase in the electron mobility (by 2 orders of magnitude). Nourdine et al. [4] synthesized fullerene-containing polystyrene-based polymers and revealed a stepwise increase in the electrical conductivity (percolation threshold) at 4 vol % of C_{60}.

A still greater effect is attained on doping of PS with another allotropic modification of carbon, graphene. A stepwise increase in the electrical conductivity occurs on introducing into the polymer graphene in an amount as low as 0.1 vol % [5].

Thus, when developing a composite material, it should be taken into account that modification may improve some properties of the polymer but simultaneously deteriorate other properties. Therefore, studies aimed to elucidate the composition-property relationship and to reveal the optimal dopant concentration become very topical.

Fig. 1 – Effect of original polystyrene films (1) and modified one (2) on *Staphylococcus aureus Rosenbach* [2]

In this study we determined the dielectric parameters (capacitance, resistivity, dielectric constant, dielectric loss tangent) of polystyrene films doped with small (up to 1 wt %) additions of fullerenes.

2. EXPERIMENTAL

In our study we used atactic polystyrene ("Aldrich", Germany) with the number-average molecular weight $M_n = 1.4\cdot10^5$ and polydispersity $M_w / M_n = 1.64$ and fullerenes C_{60} (Ltd "Fullerene Technologies", Russia). Polystyrene films and fullerene-containing polystyrene film composites were prepared as follows. First, polymer samples were dissolved in o-xylene containing C_{60} in

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the preset concentration. Then, the mixtures were stirred for 24 h, cast onto a glass support, aid dried at room temperature to fully remove the solvent. The mixture compositions; were chosen so as to ensure the fullerene content of the composite from 0.001 to 1 wt %. The film thickness was 1.00-1.13 mm.

To determine the dielectric characteristics of composites (capacitance, C, and dielectric loss tangent, tan δ) we used Solartron 1255 frequency response analyzer (UK). The numerical values of the parameters were obtained at room temperature using a two-electrode cell with round clamp electrodes 19.8 mm in diameter.

The dielectric constant (ε') of the film substance was calculated using the flat-plate capacitor formula:

$$C = \frac{\varepsilon' \varepsilon_0 S}{d} \qquad (1)$$

where S is the electrode area, d is the film thickness, and $\varepsilon_0 = 8.854 \cdot 10^{-12}$ F·m^{-1} is the electric constant. The ac resistivity was determined at a frequency of 100 Hz by the relationship

$$\rho = \left(2\pi f \varepsilon' \varepsilon_0 \tan\delta\right)^{-1} \qquad (2)$$

3. RESULTS AND DISCUSSION

The film composite samples prepared using the above-described procedure were transparent and had sufficient mechanical strength. The modified polystyrene film was light violet. The color intensity depended on the content of carbon nanoparticles in the composite. The unmodified films were colorless.

The frequency dependences of the capacitance of the formed polystyrene and composite films with different fullerene content are shown in Fig. 2. As can be seen, for all the samples studied, the capacitance does not noticeably change in the frequency range $10^4 \div 3.2 \cdot 10^6$ Hz, indicating that the composites are nonpolar or weakly polar [1, 6].

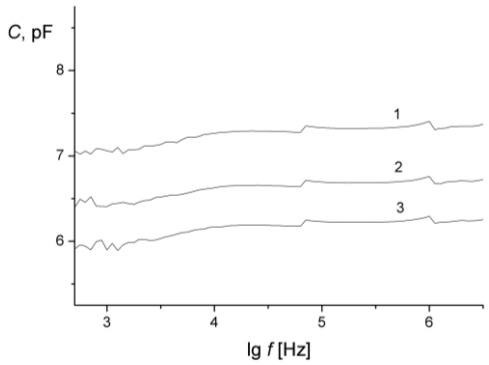

Fig. 2 – Frequency dependences of the capacitance of films with different C_{60} content. C_{60} content, wt %: 0 (1), 0.1 (2), 0.035 (3)

Fig. 3 shows the frequency dependences of the dielectric constant ε' of the composites with different fullerene content, calculated with formula (1) taking into account the measured film thickness (Table). As expected from the proportionality between C and ε', the shape of the $\varepsilon'(\log f)$ curves (Fig. 3) correlates with the shape of the $C(\log f)$ curves (Fig. 2). In the frequency interval $10^4 \div 3.2 \cdot 10^6$ Hz, the dielectric constant does not change noticeably. The ε' values obtained are well consistent with the published data. In particular, Skanavi [1] reported for unmodified polystyrene the dielectric constants in the interval 2.5÷2.9.

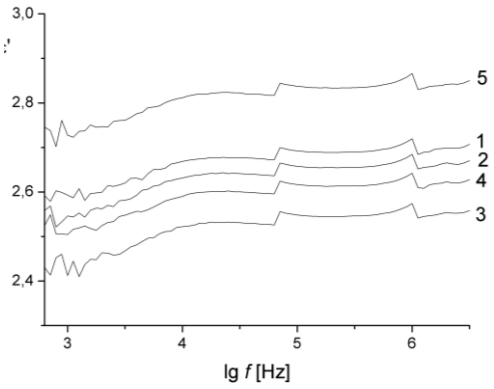

Fig. 3 – Frequency dependences of the dielectric constant, ε'. C_{60} content, wt %: 0 (1), 0.01 (2), 0.035 (3), 0.1 (4), 0.5 (5)

Table – Characteristics of PS / C_{60} composites as functions of C_{60} content

C_{60} content, wt %	d, mm	ρ, Ohm·m
0.0	1.01	$2.40 \cdot 10^{12}$
0.001	1.00	$2.25 \cdot 10^{12}$
0.010	1.08	$3.11 \cdot 10^{12}$
0.035	1.13	$9.65 \cdot 10^{11}$
0.100	1.08	$4.90 \cdot 10^{11}$
0.500	1.09	$3.14 \cdot 10^{12}$
1.000	1.05	$1.68 \cdot 10^{12}$

As seen in Fig. 3, for the composites containing 0.035 wt % of fullerenes, the dependence $\varepsilon'(\log f)$ lies below the other dependences, i.e. the dielectric constant passes through a minimum at 0.035 wt % of C_{60}.

It should be noted that the presence of similar extrema at small additions of carbon nanoparticles was also noted for other physicochemical properties of modified polymers [7, 8]. Badamshina and Gafurova [8] suggest for these facts the following explanation: whereas at low concentrations fullerene forms small clusters with fragments of molecular chains of polystyrene, with an increase in the concentration these clusters coalesce into coarse aggregates which are poorly soluble in the polymer and are inefficient as modifiers.

Nonmonotonic composition-property dependences were also observed for liquid-phase fullerene-containing systems. In particular, Ginzburg et al. [9] observed inversion of the concentration dependence of ε' for solutions of C_{60} in p-xylene, with the dielectric constant varying within the range covering several percents. This anomaly is attributed to structural changes induced by introduction of fullerenes into the aromatic solvent.

It is known that introduction of a dielectric into an electric field causes its polarization. Polystyrene is a solid amorphous dielectric containing no polar groups. In such polymers, the main kind of polarization is deformation (electronic) polarization caused by deformation of the electronic shells and appearance of induced dipoles. The contribution of the other kinds of polarization (ionic and orientation) is negligibly low because of the absence

of free ions and polar molecules.

A decrease in the polarization in time (dielectric relaxation) can be quantitatively characterized by the position of the peak in the frequency dependence of the dielectric loss tangent. For the fullerene-containing polystyrene films examined in this study, these peaks were not observed at room temperature. Apparently, the induced dipoles arise very rapidly under these conditions, and the dielectric loss is low. This is confirmed, in particular, by the results of measuring the dielectric loss tangent: In the frequency range $10^2 \div 10^6$ Hz, tan δ value is $10^{-3} \div 10^{-4}$. At higher temperatures, the frequency dependence of tanδ value can be expected to pass through a maximum. Such a maximum was found for fullerene-containing composites at glass-hyperelastic transition temperatures [10].

According to the results of previous [11] thermochemical studies, small (up to 0.01 wt %) additions of fullerenes exert plasticizing effect on polystyrene. It can lead to changes in the dielectric constant and in the dielectric loss in the polymer [6]. The lack of significant changes in these characteristics in the materials we studied can be attributed to high symmetry and nonpolarity of dopant molecules (C_{60}).

It should be noted that the estimated values of the dielectric loss tangent coincide in the order of magnitude with those for unmodified polystyrene, given in [1]. In accordance with [1], it can be stated that the dielectric loss under these temperature conditions in the low-frequency range is of ohmic nature. The polymeric materials resistivity calculated by the tanδ values (Eq. (2)) at a frequency of 100 Hz (Table), indicates that doping of polystyrene with up to 1 wt % of fullerenes does not give rise to noticeable conductivity.

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